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COMPLETE SPECIFICATION

Improvements in or relating to Shaped Cellular Polypropylene Article and Method of Making Same

5 We, HERCULES POWDER COMPANY, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 910 Market Street, City of Wilmington, Zone 99, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to the manufacture of shaped articles from polypropylene foams.

15 The fabrication of three-dimensional foamed thermoplastic compositions is well known wherein the thermoplastic composition containing a material which generates gas on decomposition, i.e., a blowing agent, is heated in an extruder or injection molding machine to a temperature which releases such gases and extruding or injecting the molten mass into a mold whereupon foaming and shaping occur essentially simultaneously. Such processes may be employed with noncrystalline thermoplastic polymers, such as polystyrene, but have been unsuccessful with polypropylene because, at the temperatures necessary to convert the expandable composition into a fluid mass, its melt viscosity is too low to withstand expansion by the gases generated from the blowing agents without rupture of the cell walls so that the foam fails to expand to fill the mold and produce the shaped article.

35 Now in accordance with this invention it has been discovered that polypropylene foams can be formed by means of extrusion or molding procedures into the shape of sheets, rods, tubes, wire and cable coatings, hollow articles such as bottles, and various molded articles, and obtain a foam of any desired density

having a uniform closed cell structure with at least 50% of the cells closed by mixing a stereoregular polypropylene with a blowing agent and an azido cross-linking agent and passing the mixture through an extruder and/or into a mold, at a temperature above the softening temperature of the mixture. 45

In carrying out the process in accordance with this invention, the stereoregular polypropylene is blended with the blowing agent and the azido cross-linking agent. Any desired means may be used for bringing about this blend. In the case of the chemical blowing agents, the azido cross-linking agent and the blowing agent may be mixed into a diluent such as acetone, which may also contain a stabilizer or other modifier for the polypropylene, and the polypropylene in finely divided form may then be added and mixed into a slurry. On evaporation of the diluent an intimate mixture of the polymer, cross-linking agent, and blowing agent is obtained which may then be used directly in an extruder or mold. The azido cross-linking agent and the chemical blowing agent may also be blended in dry form with the powdered polymer by means of a high-speed mixer such as a Waring blender or Henschel mill. This dry mix may then be used directly in the extruder or mold. When solvent types of blowing agents are employed, the stereoregular polypropylene and the azido cross-linking agent may be mixed and introduced into the extruder and the solvent blowing agent introduced directly into the extruder barrel through a vent generally located a short distance in front of the die of the extruder. The temperature in the vicinity of the die of the extruder or in the mold must be at least as high as the softening temperature of the mixture. The softening temperature of this mixture, or 50 55 60 65 70 75 80

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blend, will depend upon whether the blowing agent is a solvent type or a chemical type. Thus, with a solvent type, the polypropylene will at least partially dissolve so that the softening temperature of the blend can be as low as 135° C. On the other hand, with a chemical blowing agent, the softening temperature of the blend will be the melting point of the polymer and, hence, will be above about 165° C. Accordingly, the temperature within the extruder or mold must be at least as high as the softening temperature of the mixture passing through the extruder. The exact temperature to be used for the total operation will depend upon the cross-linking and blowing agents used and the residence time in the extruder or mold.

When the mixture of polypropylene, cross-linking agent, and blowing agent is heated in an extruder, particularly in the case of an extruder with a temperature gradient, blowing may be at least partially effected at the low temperature in the first zones of the extruder and cross-linking will be effected at the higher temperature in the final zones of the extruder, in which case the cross-linking is effected immediately prior to the expansion that takes place when the mass leaves the extruder at the die. It is essential that the cross-linking must have occurred at the time that expansion takes place at the die of the extruder or simultaneously therewith. Hence, the temperature in the final zone of the extruder must be sufficient to complete the cross-linking of the polypropylene and to release the gas from the blowing agent.

Foamed sheets can be prepared by this extrusion procedure and by using dies with suitable dimensions, sheets of varying thickness can be produced. Such sheets find utility in a variety of applications such as thermal insulations in environments where exposures to elevated temperatures and/or organic solvents would be encountered. The excellent physical properties imparted by the closed cells of these sheets make them useful in thinner dimensions as water-resistant substitutes for cardboard and in such applications as folding cartons and other packaging applications, and notebook covers. These extruded sheets may be shaped by any of the well-known techniques such as the thermoforming and vacuum-forming.

Wire and cable coatings produced by extruding the foam onto the wire or cable have improved dielectric and physical properties as a result of their more uniform closed cell structures. For use in wire coating and other electrical conductor insulations, the foams will preferably have at least 70% of the cells closed and densities of less than 40 lbs./cu. ft. These coatings will preferably have densities below about 35 lbs./cu. ft. and are capable of being employed at much lower densities, which improves the dielectric

properties, flexibility, and offers economies in the production of coated wire and cable.

Hollow articles made of polypropylene foam can be produced by blowing a parison, the plastic composition of which comprises stereoregular polypropylene, a blowing agent, and an azido cross-linking agent as described above. It was most unexpected that by extruding a parison from an expandable polypropylene composition that it would be possible to obtain walls of sufficient strength to enable the expansion of the parison without rupturing the parison wall. Bottles or other blown hollow articles of foamed polypropylene can be produced in accordance with this invention in which the density of the foam wall can be as low as 30 lb./cu. ft. or less and which have a uniform cell structure with at least 50% of the cells closed and preferably with more than 70% closed cells. As the cellular parison emerges from the extruder die it is fed by gravity between the mold cavities in an open position. As the mold closes around the parison, one end is pinched to close the end and air pressure is then introduced which expands the parison to the shape of the mold cavity. The applied air pressure to expand the parison will be variable depending on the wall thickness of the parison and the extent to which it must be expanded to fill the mold cavity. Any of the standard blow molding apparatus generally used for the manufacture of hollow articles may be used in producing the foam bottles.

The blown cellular bottles and other hollow shapes prepared according to this invention have a number of advantages over similar shapes prepared from unexpanded polypropylene. The saving in weight is of considerable economic advantage, both in the quantity of plastic employed and in reduced shipping and handling costs. The cellular structure also markedly improves the impact strength of the polypropylene and thus overcomes the most serious deterrent to the use of this plastic in bottles. When hollow shapes such as bottles are used as containers for liquids, a predominantly closed cell structure, as obtained in this invention, is absolutely necessary to prevent leakage of the liquid and its vapors. Other advantages of these cross-linked expanded structures are their greater resistance to solvents and other characteristics which permit the packaging of a wider variety of products than would otherwise be possible and in their heat resistance which permits sterilization of containers for such uses as milk, pharmaceuticals and cosmetics.

Shaped articles can also be produced by externally applying a mechanical force to the male portion of a matched mold pair, onto a polypropylene composition contained in the female portion of the mold, wherein the polypropylene composition comprises the above described mixtures of stereoregular polypropy-

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lene, a blowing agent, and an azido cross-linking agent, and said composition is heated to a temperature above the softening point of the composition and sufficient to release the gas from the blowing agent and to effect cross-linking of the polypropylene. It was entirely unexpected to find that an expandable polypropylene composition could be fabricated. When the cross-linking agent is not employed, as described in this invention, the molten mass is largely open celled due to rupture of the cell walls by the expanding gases; and, furthermore, the foam collapses to a fraction of its original volume during cooling. Thus, when such a foamed mass is shaped by application of pressure by the plunger, the resulting structure is considerably higher in density than the original foam, is non-uniform in cellular structure and is predominantly open celled.

One method of carrying out the preparation of such molded articles is to extrude, or introduce by and other means, the mixture of stereoregular polypropylene, blowing agent and azido cross-linking agent, in a molten condition into an open cavity of a mold whereupon foaming of the mass occurs. It is then shaped into a three-dimensional structure by the application of pressure from a plunger of suitable shape being forced into this cavity. By such application of pressure of the plunger, the foamed plastic mass retains its closed cell structure, but is caused to flow into the shape of the free space between the plunger and the mold. The density of the resulting shaped articles is essentially the same as that of the original foamed mass before shaping.

The temperature used for the molding operation must be sufficient to convert the plastic foam into a condition such that it is fluid under the pressure applied by the plunger. The expansion of the gases within the foamed composition should be essentially complete before the application of such pressure. Some cross-linking of the polymer must also have occurred at this time in order to prevent cell rupture, but need not have been completed as completion of the cross-linking reaction can be effected by subjecting the shaped article to additional heating. The exact temperature to be employed will, as previously described, depend on several factors, but always will be at least above the softening temperature of the mixture of the polypropylene, cross-linking agent and blowing agent.

An alternate method of producing these molded articles is to place a quantity of unexpanded, or partially expanded, pellets made of the mixture of stereoregular polypropylene, blowing agent, and cross-linking agent into the aforementioned mold cavity and heating said mold and pellets to a temperature above the softening temperature of the pellets and sufficient to effect further release and expansion of the blowing gases and fill the mold, to complete the cross-linking of the polypropylene, and to fuse the expanded pellets into an integral cellular structure. While the pellets are in this softened state, the plunger is forced into the cavity as described above which causes the molten plastic to flow into the shape of a three-dimensional article as determined by the relative shapes of the male and female portions of the matched mold set.

In addition to their use in the preparation of molded shaped articles, the partially expanded and cross-linked polypropylene pellets can be used in many other processes of preparing articles made of cellular materials as, for example, in the manufacture of foam sheets, wire and cable coatings and other electrical conductor insulation, the manufacture of blown articles such as tubing and bottles, and other such applications.

The partially expanded polypropylene pellets are prepared by intimately mixing stereoregular polypropylene, an azido cross-linking agent, and a blowing agent and passing the mixture, or blend, through an extruder at a temperature above the softening temperature of the polymer, to form a partially cross-linked and partially expanded strand which is then chopped into pellets. The amount of this partial cross-linking and blowing must be such that less than about 90% of the potential blow of the mixture has been effected, preferably less than about 75% and more preferably from about 50% to about 75%. This partial blowing and cross-linking may be effected by a variety of means as, for example, by adjusting the time of heating, such as the residence time in an extruder and the temperature at which the partial expansion and cross-linking are carried out.

Any stereoregular polypropylene may be used to prepare the foams in accordance with this invention, but generally polypropylenes having a reduced specific viscosity (RSV) of from 1 to 5 and, more preferably, 2 to 3, are used, said reduced specific viscosity being determined on a 0.1% solution of the polymer is decahydronaphthalene at a temperature of 135° C.

Any of the well-known chemical blowing agents may be used in the preparation of the foams in accordance with this invention as, for example, azo bis(formamide), diazoaminobenzene, N, N¹ - dinitrosopentamethylene tetramine, N, N¹ - dimethyl - N, N¹ - dinitrosoterephthalamide, p, p¹ - oxy - bis(benzene sulfonyl semicarbazide), azo bis(isobutyronitrile), p, p¹ - oxy - bis(benzene sulfonyl hydrazide), p, p¹ - diphenyl - bis(sulfonyl hydrazide), benzene-sulfonyl hydrazide and m - benzene - bis(sulfonyl hydrazide). Any of the well-known solvent blowing agents may also be used in this invention as, for ex-

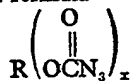
ample, monochlorotrifluoromethane, monochlorodifluoromethane, dichlorotetrafluoroethane, trichloroethylene chloroform, carbon tetrachloride, and low boiling hydrocarbons such as butane, pentane and hexane. Accordingly, any compound which decomposes or volatilizes to yield at least one mole of gas per mole of blowing agent at a temperature of 190° C. or less may be used.

Any azido cross-linking agent may be used in the preparation of the extruded and/or molded polypropylene foams in the process of this invention. Thus, any poly(sulfonazide), i.e., any compound having the general formula



where R is an organic radical inert to the cross-linking reaction and x is an integer greater than 1, can be used in the process of this invention. Preferably, x will be an integer from 2 to 100 and R will be selected from the group of organic radicals consisting of alkylene, arylene, aralkylene, and alkarylene radicals; however, these radicals can also contain ether, alcohol and halogen, groups which are inert to the cross-linking reaction. Exemplary of the poly(sulfonazide)s that may be used are 1, 7 - heptane - bis(sulfonazide), 1, 10 - decane - bis(sulfonazide), 1, 11 - undecane - bis(sulfonazide), 1, 12 - dodecane - bis(sulfonazide), 7 - oxa - tridecane - 1, 13 - bis(sulfonazide), 6 - thiaundecane - 1, 11, - bis(sulfonazide); chloro - aliphatic poly(sulfonazide)s such as the poly(sulfonazide) produced from a chloro- and sulfochlorinated mixture of petroleum hydrocarbons and containing at least one chlorine atom and at least two sulfonazide groups per molecule; 1, 9, 18 - octadecane - tris(sulfonazide), poly(ethylene sulfonazide), poly(sulfonazido - methylstyrene), 1, 3- and 1, 4 - bis(sulfonazido - methyl benzene), 1, 3 - benzene bis(sulfonazide), 1 - octyl - 2, 4, 6 - benzene tris(sulfonazide), 4, 4¹ - diphenylmethane bis(sulfonazide), 4, 4¹ - diphenyl ether bis(sulfonazide), 4, 4¹ - bis - octadecyl biphenyl - 3, 5, 3¹, 5¹ - tetra(sulfonazide), 4, 4¹ - diphenyl disulfide bis(sulfonazide), 1, 6 - bis(4¹ - sulfonazidophenyl) hexane and 2, 7 - naphthalene bis(sulfonazide).

Another class of azido cross-linking agents that may be used are azidoformates which have the general formula



where x is at least 1, preferably from 1 to 100, and R is an organic radical, inert to cross-linking reactions, containing at least one carbon atom per azidoformate group. Exemplary of these azidoformates are the alkyl azidoformates such as n-octadecyl azidoformate, tetramethylene - bis(azidoformate), pentamethylene - bis(azidoformate); the cyclic alkyl azidoformates such as 2 - (1 - p -

methyl - 8 - yloxy) ethyl azidoformate; the aromatic azidoformates such as phenyl azidoformate, *z*, *z*¹ - p - xylylene - bis(azidoformate), 2, 2 - isopropylidene - bis(p, p¹ - phenyl azidoformate); the azidoformate ethers such as 2, 2¹ - oxydiethyl - bis(azidoformate), 2, 2¹ - oxydipropyl - bis(azidoformate), 2, 2¹ - ethylenedioxydiethyl - bis(azidoformate), the tetraazidoformate of pentaerythritol - propylene oxide adduct, the azidoformate thioethers such as 2, 2¹ - thiodiethyl - bis(azidoformate) and 4, 4¹ - thiodibutyl - bis(azidoformate).

Still another class of azido cross-linking agents that can be used are the aromatic polyazides having the general formula R(N₃)_x where R is an aromatic grouping inert to the cross-linking reaction, and x is an integer greater than 1. Preferably x will be an integer from 2 to 200 and R will be selected from the group of organic radicals consisting of arylene and alkarylene radicals. Exemplary of the aromatic polyazides useful in this invention are m- phenylene diazide, 2, 4, 6, - triazidobenzene, 4, 4¹ - diphenyl diazide, 4, 4¹ - diphenylmethane diazide, 4, 4¹ - diazido diphenylamine, 4, 4¹ - diazido diphenylsulfone, 2, 7 - diazidonaphthalene and 2, 6 - diazido - anthraquinone. Thus, any compound having at least one azido group in the molecule and preferably two or more can be used as the azido cross-linking agent to prepare the extruded polypropylene foams of this invention.

The amount of the azido cross-linking agent utilized in the preparation of these cellular polypropylene articles can be varied over a wide range. It must be an amount that is sufficient to prevent rupture of the cell walls when the foaming action takes place. Generally, it will be an amount of from about 0.01% for a final foam of 40 to 50 lbs./cu. ft. density up to about 2% by weight of the polymer for foams below 5 lbs./cu. ft. density, although higher concentrations can be used if desired. The amount of blowing agent incorporated will obviously depend upon the degree of blowing desired; that is, the density desired for the final foamed product and the types of blowing agent used.

Many variations can be made in the process of this invention and in the extruded or molded compositions of this invention without departing from the invention. Thus, there can be incorporated in the polypropylene used or in the preparation of the blends of polypropylene, blowing agent, and cross-linking agent, such additives as light and heat stabilizers for the polypropylene, dyestuffs and pigments, flame retardants, including organic and inorganic flame retardants, such as chlorinated paraffin wax, antimony oxide and other such materials. For many applications it is desirable to increase the flexibility of the extruded foams by incorporating in the foam an elastomer. This may be done by mixing

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a synthetic or natural rubber with the blend of polypropylene, cross-linking agent and blowing agent and extruding said mixture. Exemplary of the elastomers that can be so

- 5 incorporated are ethylene-propylene copolymer rubbers, ethylene-propylene-diene terpolymer rubbers, polyisobutylene, etc. Many other variations will be apparent to those skilled in the art.
- 10 The following examples will illustrate the preparation of extruded and/or blown or molded cross-linked polypropylene foams in accordance with this invention. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

- A dry blend of 100 parts of stereoregular polypropylene having an RSV of 2.4, 1 part of azo bis (formamide) and 0.1 part of 1, 10 - decane - bis(sulfonazide) was extruded, through a 1-1/4 inch extruder with a temperature profile of 149° C. in the first zone and 200 °C. in the second and third zones, through a six-inch slit die at 210° C., and into a water bath about 4 inches away. The resulting foamed sheet was completely foamed and had a fine closed cell structure with greater than 70% of the cells closed. It had an approximate density of 30 lbs./cu. ft.

EXAMPLE 2

- A mixture of 100 parts of stereoregular polypropylene having an RSV of 2.7, 0.1 part of tetramethylene bis(azidoformate) as cross-linking agent, and 1.0 part of azo bis (formamide) as blowing agent, was blended on a two-roll mill for 5 minutes at 166° C. After cooling, the milled blend was chopped in a plastic cutter to a nominal particle size of 1/8 inch diameter. The particles were then fed into a 1-inch, 6:1 ratio (length: diameter) extruder with barrel and die heated to 216° C. and operating at low speed. The extruded strand was collected in 6- to 8-inch lengths and allowed to cool in air. The foamed strands so prepared had a uniform closed cell structure and an approximate density of 30 lbs./cu. ft.

- When the example was duplicated, except that tetramethylene bis(azidoformate) cross-linking agent was omitted, the foamed strands had a very non-uniform structure and an approximate density of 37 lbs./cu.ft.

EXAMPLE 3

- A dry blend of 100 parts of stereoregular polypropylene having an RSV of 2.7, 0.75 part of azo bis (formamide) and 0.1 part of 1, 10-decane-bis(sulfonazide) was fed into an extruder operating with a temperature profile of 177° C. at the feed end and 204° at the die. The plastified material was fed into a wire coating die where it was deposited on 14-gage wire which had been preheated to 190° C. and travelling at

500 ft./min. After emerging from the die, the coated wire travelled 4 to 5 inches through ambient air to a water bath heated to 80° C. Foaming of the coating was largely completed by the time the wire emerged from the die. The resulting foamed insulation had a density of approximately 30 lbs./cu. ft. and possessed a fine and closed cell structure in which more than 70% of the cells were closed. When wire was coated by the same procedure, but omitting the cross-linking agent, such a low density could not be obtained with this high level of closed cells.

EXAMPLE 4

A mixture of 85 parts of stereoregular polypropylene having an RSV of 2.5, 15 parts of polyisobutylene (molecular weight of about 100,000), 0.5 part of azo bis (formamide), 0.05 part of 1,10-decane-bis(sulfonazide) and 0.20 part of Santonox [4, 4' - thiobis(6 - tert - butyl - m - cresol)] as a stabilizer was placed on a two-roll mill at 166° C. and mixed for 10 minutes with repeated cross-cutting and end-rolling. The blend was then sheeted from the mill, cooled and chopped into granules.

These pellets were fed into an extruder operating with a temperature profile of 180° C. at the feed end and 210° C. at the die. The plastified material was fed into a wire coating die where it was deposited onto a 20-gage wire which had been preheated to 190° C. and travelling at 500 ft./min. After emerging from the die, the coated wire travelled through 4 to 5 inches of air to an 80° C. water bath. The resulting foamed insulation had a density of approximately 35 lbs./cu. ft. and had a fine, closed cell structure with more than 70% of the cells closed.

EXAMPLE 5

A partially expanded composition in the form of expandable pellets was prepared by mixing in acetone 100 parts of a stereoregular polypropylene having an RSV of 2.7 with 0.25 part of 1,10-decane-bis(sulfonazide) and 2.0 parts of azo bis(formamide), evaporating the acetone and passing the mixture through an extruder at 180° C. to yield a partially blown strand. This strand which was about 65% expanded was chopped into pellets. The pellets were packed into a closed mold which was heated for 15 minutes at 204° C. On opening the mold, the shaped article had a tough surface and a cross-section of it showed it to be free of voids and to have a uniform cell structure with more than 50% of the cells closed. The approximate density of the foam was 20 lbs./cu. ft.

EXAMPLE 6

A dry blend of 100 parts of a stereoregular polypropylene having an RSV of 2.7, 2 parts of azo bis (formamide) and 0.5 part of 1,10-

decane-bis(sulfonazide) was extruded in a 1-1/4 inch extruder operating at 200—204° C. The expanding composition emerging from the extruder was collected in the female cavity of a cup mold which had been preheated to 193° C. When the precalculated weight of expanding polypropylene had been collected, the male plug was forced into place and the mold was allowed to cool. The expanded polypropylene cup so formed had a uniform cell structure with more than 50% of the cells closed and a density of 20—25 lbs./cu. ft. The cup had smooth surfaces both inside and out.

EXAMPLE 7

The dry blend used in Example 6 was extruded at 177° C. into strands. These partially expanded and cross-linked strands were chopped into pellets. The cup mold was preheated to 193° C., a calculated weight of the expandable pellets was placed in the cavity and the plug was forced into place. The mold was then placed in a press, heated to 204° C., for 10 minutes, with the pressure maintained so that the mold closed completely as the pellets softened and expanded. The finished cup had smooth surfaces. The foam was uniform in structure with more than 50% of the cells closed, and it had a density of 20—25 lbs./cu. ft.

EXAMPLE 8

In this example a chloroaliphatic poly(sulfonazide) was used as the cross-linking agent. It was prepared as follows: Sulfur dioxide (300 ml. of gas per minute) was passed into a solution of 31.2 grams of a commercial mixture of hydrocarbons containing 11 and 12 carbon atoms per molecule in 200 ml. of carbon tetrachloride. After five minutes the mixture was exposed to the light from an ultraviolet lamp three inches from the reactor, and chlorine was passed in at the rate of 77 ml. per minute. The combined gases were passed in for 223 minutes while holding the temperature at 25° C. After turning off the light and the gases, the solvent was removed under vacuum whereby there was obtained a viscous oil which, on analysis, was found to contain 16.6% of sulfur and 29.2% of chlorine. To a solution of 11.2 g. of this chlorosulfonated hydrocarbon in 150 ml. of acetone was added drop-wise a solution of 7.8 g. of sodium azide in 25 ml. of water while stirring with a magnetic stirrer. After stirring for one hour at room temperature, the reaction mixture was heated at 60° C. for 3 hours. Stirring was continued for 16 hours at room temperature, after which the solvent was removed and the resulting mixture was diluted with 150 ml. of chloroform. The solution so obtained was washed with water and dried. On removing the diluent there was obtained 9.7 g. of an

amber viscous oil which, on analysis, was found to contain 5.4 milliequivalents of azide per gram and 11.7% chlorine.

A partially expanded composition in the form of expandable pellets was prepared by mixing in acetone 100 parts of a stereoregular polypropylene having an RSV of 2.4 with 0.25 part of the above chlorohydrocarbon poly(sulfonazide), and 1.5 parts of azo bis(formamide) as blowing agent, evaporating the acetone and passing the mixture through an extruder at 193° C. to yield a partially blown strand. This strand was then chopped into pellets. These pellets which were about 70% expanded were packed into a closed mold which was heated for 15 minutes at 204° C. At this temperature the polymer was further cross-linked and simultaneously expanded to completely fill the mold. On opening the mold, the cross-linked, foamed polypropylene was observed to possess a tough surface with a void-free, uniform internal cell structure with more than 50% of the cells closed. The foamed article had an approximate density of 20 lbs./cu. ft.

EXAMPLE 9

A mixture of 99.58 parts of stereoregular polypropylene having an RSV of 2.4, 0.38 part of azo bis(formamide), and 0.04 part of 1,10-decane-bis(sulfonylazide) was extruded through a 1.5-inch extruder of L/D ratio of 24:1. The molten polymer blend passed through a tube-forming cross-head and then through an annular die attached to the cross-head. The land of the die was 1.6 inches long and 11/16 inch inside diameter. The mandrel inside the die extended to the end of the die and had an outside diameter of 1/4 inch. Thus, the die and mandrel were separated by an annulus whose width was 7/32 inch. The temperature of the molten polymer blend as it passed through the cross-head was 182° C. The extruded tube, or parison, moved vertically downward between the opened halves of a 4 oz. Boston-round bottle mold. The bottle mold was jacketed and cooled with 18° C. water. After extruding a parison of suitable length, the extruded was stopped, the mold closed around the parison and air, at a pressure of 40 p.s.i., was blown through the die mandrel to expand the parison to the shape of the bottle mold. The mold was held closed for 45 seconds to cool the molded bottle which was then removed. The wall of the bottle so produced had a fine, uniform, cell structure with more than 70% of the cells closed and had a bulk density of 38 lbs./cu. ft.

Attempts to prepare bottles from a control foam where no cross-linker was used in the preparation of the foam failed due to rupture of the cell walls and blowing out of the wall of the parison. It was not possible to expand the parison to the shape of the bottle mold.

EXAMPLE 10

A bottle was blown by the general procedure described in Example 9. In this case a mixture of 76.68 parts of a stereoregular polypropylene having an RSV of 2.4, 23 parts of a stereoregular polypropylene having an RSV of 2.7, 0.29 part of azo bis(formamide) and 0.03 part of 1,10-decane-bis(sulfonylazide) was extruded. The inside diameter of the die used in this example was 7/16 inch instead of 11/16 inch which reduced the annulus width to 3/32 inch so as to make a thinner walled bottle. The parison was expanded was 15 p.s.i. pressure and the bottle was cooled for 30 seconds before opening the mold. The bottle so obtained was well formed, and the bottle wall had a bulk density of 32 lbs/cu. ft. with more than 70% of the cells closed.

EXAMPLE 11

A bottle was blown by the general procedure described in Example 9. In this case a mixture of 90 parts of stereoregular polypropylene having an RSV of 2.5, 10 parts of polyisobutylene (molecular weight of about 100,000), 0.5 part of azo bis(formamide), 0.05 part of 1,10-decane-bis(sulfonazide), and 0.20 part of Stantonox [4,4'-thiobis(6-tert-butyl-m-cresol)], as a stabilizer, was placed on a two-roll mill at 165° C. and mixed for 10 minutes were repeated cross-cutting and end-rolling. The blend was then sheeted from the mill, cooled, and chopped into pellets.

These pellets were fed into the extruder and a parison was extruded and blown as described in Example 9, The wall of the bottle so produced had a uniform, fine, closed cell structure with more than 70% of the cells closed and an apparent density of 35 lbs./cu. ft.

Our copending application No. 36980/63 (1022051) describes and claims a cross-linked stereoregular polypropylene foam having a uniform cell structure in which at least 50%, preferably at least 70%, of the cells are closed.

WHAT WE CLAIM IS:—

1. A shaped article comprising a cross-linked stereoregular, polypropylene foam having a uniform cell structure in which at least 50% of the cells are closed.

2. An article as defined in Claim 1 consisting of an insulated electrical conductor having a wire coated with a cross-linked polypropylene foam having a uniform closed cell structure with at least 70% of the cells closed and a density of less than 40 lbs./cu. ft.

3. An article as defined in Claim 1 consisting of an insulated electrical conductor having a wire coated with a cross-linked and

foamed blend of polypropylene and an elastomer, which foam has a uniform closed cell structure with at least 70% of the cells closed and a density of less than 40 lbs./cu. ft.

4. A process of preparing the article defined in any one of Claims 1, 2 or 3, which comprises heating a mixture of stereoregular polypropylene, a blowing agent, and an azido cross-linking agent, to at least the softening temperature of the mixture and sufficient to release the gas from said blowing agent and to effect cross-linking of said polypropylene, and forming the foam into a shaped article.

5. The process of claim 4 wherein the mixture is heated in an extruder.

6. The process of Claim 4 wherein the mixture is heated in a closed mold.

7. The process of Claim 4 wherein an elastomer is added to the mixture that is heated.

8. The process of Claims 5 or 7 wherein the mixture is extruded through a slot die to form a sheet of foam.

9. The process of Claims 5 or 7 wherein the mixture is extruded onto an electrical conductor.

10. The process of Claims 5 or 7 wherein the mixture is extruded into a parison and said parison is then blown into a hollow mold.

11. The process of Claim 6 which comprises filling the mold of the desired shape with partially expanded pellets of the mixture of stereoregular polypropylene, blowing agent, and azido cross-linking agent, closing said mold and heating said mold and expandable pellets to a temperature above the softening point of said pellets, said temperature being sufficient to release the gas from said blowing agent, to complete the cross-linking reaction, and to fuse the expanded pellets into an integral cellular structure.

12. The process of Claim 11 wherein said mold and expandable pellets are heated to a temperature of from 165° C. to 275° C., whereby essentially complete expansion and cross-linking of the polypropylene are effected and the pellets are fused into an integral cellular structure.

13. A shaped article as claimed in Claim 1, comprising a stereoregular polypropylene foam substantially as described herein.

14. A process as claimed in Claim 4 of preparing a shaped article comprising a stereoregular polypropylene foam, the said process being substantially as described herein.

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